Hydrothermal synthesis, characterization and magnetic properties of BaFe₂O₄ nanostructure as a photocatalytic oxidative desulfurization of dibenzothiophene

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Abstract

In this work BaFe₂O₄ nanostructure have been produced hydrothermal method using PTSA (*p*-toluenesulfonic acid) as fuel. The as-produced nanostructures were characterized by techniques like X-ray powder diffraction (XRD), Fourier transform infrared spectra (FT-IR), Energy-dispersive X-ray spectrometry (EDS), Scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). The photocatalytic oxidation of dibenzothiophene (DBT), benzothiophene (BT) and dodecanethiol (RSH) in model oil was studied at room temperature (30°C) with catalyst. The system contained BaFe₂O₄, H₂O₂, and acetonitrile liquid, UV- Vis lamp which played vitally important roles in the photocatalytic oxidative desulfurization. Especially, the molar ratio of H₂O₂ and sulfur (O/S) was only 3:1, which corresponded to the stoichiometric reaction. The sulfur removal of DBT-containing model oil with BaFe₂O₄ could reach 96.6%. The system could be recycled seven times without a significant decrease in photocatalytic activity.

Keywords: BaFe₂O₄; Hydrothermal; Photocatalytic; Desulfurization; Nanostructures.

1. Introduction

Nanostructure materials have various and attractive application in different fields such as superconductors, photocatalytic, supercapacitors and nanoelectronics [1-3]. The properties of nanomaterials depend on their morphology, composition, size and size distribution. Acid rain is from SO_x by combustion of sulfur compounds. Many developed countries have planned to achieve little-to-no sulfur fuels (S-content<10 ppm) to reduce the emission by Sox. It is necessary to develop alternative ultra-deep desulfurization processes such as adsorption [4-7] extraction [8-11] oxidation [12-16] and bioprocesses [17-21]. As one of the processes, photocatalytic oxidative desulfurization is promising because of high catalytic activity, safety and low energy and recycling [22, 23]. As one of semiconductor materials such as BaFe₂O₄ is an important photocatalyst based on its high photostability, photoactivity and inexpensiveness. BaFe₂O₄ can achieve applications in the decomposition of sulfur compounds with UV-VIS radiation. Recently, is reported extraction and catalytic oxidative desulfurization (ECODS) in ionic liquids, which exhibited high sulfur removal [24-26]. BaFe₂O₄ has high capacity of magnetization and high chemical stability as well as photocatalytic properties [27]. The degradation by photocatalysis is based on the irradiation of a photocatalyst [28].

In this paper, the target is to produce of BaFe₂O₄ and to present a high efficiency photocatalytic desulfurization system containing BaFe₂O₄, ionic liquid and H₂O₂. It was found that DBT could be deep removed by the BaFe₂O₄ combined with only stoichiometric H₂O₂ and conventional acetonitrile under UV-Vis light. The performance of the recycled catalyst was also detected. All of the oxidation methods used to date have drawbacks of one form or another, e.g. poor activity, poor selectivity, loss of catalyst or cost of catalyst. The aim of the present work was to produce a highly selective, inexpensive and/or recoverable catalyst for the oxidation of sulfur compounds present in oil. The oxidant had to be inexpensive and give by-products that would not adversely affect the product or cause environmental problems. Morphology and purity of BaFe₂O₄ was studied by using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX),

Transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). Vibrating sample magnetometer (VSM) was used to study the magnetism properties of BaFe₂O₄ samples.

2. Experimental

2.1. Materials and characterization

Ba(NO₃)₂, Fe(NO₃)₃·9H₂O and PTSA were purchased from Merck Company (pro-analysis) and used without further purification. FT-IR spectra were obtained on a Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400-4000 cm⁻¹. XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K α radiation (λ = 1.54 Å, operated on 35 mA and 40 kV current). TEM image was obtained on a JEM-2100. SEM images were taken by using a field-emission scanning electron microscope (FE-SEM, HITACHI S4160, Japan). EDS analyses were studied by XL30, Philips microscope. Magnetic properties were measured using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan). Ultraviolet-visible (UV-VIS) spectrum was performed on UV-2450 spectrophotometer in acetonitrile.

2.2. Synthesis of barium monoferrite nanostructure

Iron (III) nitrate solution were added with mole ratio (Ba⁺²/PTSA) 1, 2 and 3 under strong magnetic stirring at 60 °C for 30 min. BaFe₂O₄ was made by autoclaving mixtures of the metal nitrates at 332 °C/5 h, which was then annealed to give the pure crystalline product. Followed by, thermal dehydration done and the obtained powder disinterred at 800, 900 and 1000 °C for 2 h (Table 1).

2.3. Photocatalytic oxidative desulfurization from oil

Model oil was prepared by dissolving dibenzothiophene (DBT), benzothiophene (BT) and dodecanethiol (RSH) in the n-octane, with a corresponding Scontent of 500, 250 and 250 ppm, respectively. The four types of model oil were all with 4,000 ppm tetradecane as the internal standard. The photocatalytic reactor consisted of a quartz glass with a circulating water jack and a UV-Vis. The photocatalytic oxidative desulfurization procedure was run as follows: 5 mL of model oil, 0.005 g of catalyst, 1mL of the conventional IL were added into the reactor and 0.156

mmol H₂O₂ (30 wt%) was injected. The resulting mixture was stirred at 30 °C for 2 h, and after the reaction Total sulphur test was studied by sulphur meter (RX 360SH Tanaka).

3. Results and discussion

3.1. SEM images of BaFe₂O₄ nanostructures

The morphology of the BaFe₂O₄ micro/nanostructures is examined by SEM (Fig. 1). Fig. 1a shows the related image of blank sample that prepared without using PTSA; it is observed that the structure was agglomerated (sample no. 1). SEM images of the samples prepared with various ratio of PTSA:Ba(NO₃)₂ 1:1 (sample no. 2), 1:2 (sample no. 3), 1:3 (sample no. 4) are shown in Fig. 1b–d, respectively. In Fig. 1a-c structures and particle-size distribution are irregular, but uniform shapes are shown in Fig. 1d (100-200 nm). Therefore, 1:3 ratio is known the best. Fig 2a, b, and c shows the scanning electron microscope (SEM) images of the samples calcined at 800⁰C and 900⁰C and 1000 °C for 2h, respectively. The result shows that the mean particle size increases with an increase in the calcination temperature. At 800 °C the particles are isolated completely and their size is 10 nm (Fig. 2a). When the temperature reaches to 900 °C, the particles connect to each other in the special orientations that originate from certain configuration PTSA which use as anti-aggregation (Fig. 2b) and create interlaced rods. By increasing the temperature to 1000 °C, isolated structures are observed that include 100 nm particles.

3.2. X-ray diffraction

Fig.3 shows the XRD patterns of the samples calcined at 800⁰C (sample no.4) , 900⁰C(sample no.5) and 1000 °C(sample no.6) for 2h, respectively. An orthorhombic BaFe₂O₄ phase, as indicated by the open circles (Fig. 3), was found to be formed at the temperatures 1000 °C. The crystallinity was found to increase with increasing calcination temperature, higher crystallinity is well known to yield a high density of active catalytic sites, thereby yielding efficient photocatalysts [29]. The crystallite sizes were estimated from the full width at half maxima (FWHM) of the main XRD peak (Fig. 3) with a (212) orientation by using the Scherrer's equation [30]; $D = 0.9\lambda / \Delta 2\theta \cos\theta$; Where λ is the wavelength of the X-ray radiation (Cu K α with $\lambda = 1.54 \text{ \AA}$), $\Delta 2\theta$ is the FWHM of the

peak (in radians) corrected for instrumental broadening, θ is the Bragg angle, and D is the crystallite size ($\text{\AA}$). The crystallite sizes for all the samples are nearly the same (52 nm), revealing their nanocrystalline dimension.

3.3. FT-IR and EDX analysis

[Fig. 4a](#) shows the FT-IR spectrum of the sample no. 6. The absorption characteristic peaks of BaFe_2O_4 were at 449.36 cm^{-1} , 555.24 cm^{-1} , and 603.25 cm^{-1} . However, the free O–H stretch vibration of the carboxyl group around 3444 cm^{-1} . An additional confirmation for our assignment is the O–H in-plane-bend vibration at about 1026 cm^{-1} , which is typical for a non-hydrogen bonded carboxylic OH group. Similarly, the absorption peak of the S=O stretch vibrations around 1620 cm^{-1} is almost identical for the PTSA, but is substantially red shifted if it is involved in hydrogen bonds. From the result it can be inferred that the reaction of PTSA complex is complete. The band C–H bending vibrations at about 1380 cm^{-1} mainly shown. In the EDS spectrum of BaFe_2O_4 obtained from sample 6, Ba, Fe, and O elements are detected ([Fig. 4b](#)).

3.4. Magnetic properties

The magnetic properties of materials were investigated by VSM. The magnetic hysteresis loops were depicted in [Fig. 5](#) Magnetic hysteresis loop at room temperature has been recorded for sample no. 4, 5 and 6 respectively. Although H_c will increase with a decrease in grain size, especially below the single domain size [\[31\]](#), there is also a minimum grain diameter for maximum coercivity. This is $0.1\text{ }\mu\text{m}$ for Ba-ferrite, as at smaller diameters the H_c decreases greatly as the ferrite tends towards the superparamagnetic state, which has a coercivity of zero at around 10 nm [\[32\]](#).

3.5. TEM image

Fig. 6 shows the TEM images of barium monoferrite nanostructures (sample no.6). The TEM images show barium monoferrite nanostructures with an average size of 25 nm and aggregated nanostructures with spherical-like shape are achieved.

3.6. Catalytic activity

3.6.1. Effect of different systems on sulfur removal

Different systems on sulfur removal are shown in Table 2. The photocatalytic desulfurization of DBT-containing in model oil only by BaFe_2O_4 was examined. When H_2O_2 was added into the model oil, the sulfur removal increased. H_2O_2 could not make a good contact with DBT. With acetonitrile added into the above system, sulfur removal rose sharply. This result shows that the synergistic effect of BaFe_2O_4 , H_2O_2 , and acetonitrile was very favorable for the improvement of the photocatalytic activity of DBT oxidation.

3.6.2. Effect of UV light on sulfur removal

Comparing oxidation of DBT with UV-Vis irradiation and without UV-Vis, sulfur removal with BaFe_2O_4 photocatalysts is shown in Fig. 7a. With UV-Vis irradiation, the sulfur removal was 92.0% in 100 min, while without UV-Vis irradiation, the sulfur removal could reach 61.4%. When BaFe_2O_4 was irradiated by UV-Vis light, the conduction band electron (e^-) and valence band holes (h^+) were generated. The e^- could react with electron acceptor H_2O_2 to form hydroxyl radicals ($\text{HO}\cdot$) which could oxidize DBT to corresponding sulfones [33]. So the sulfur removal of the system with UV-Vis was higher than the system without UV-Vis.

3.6.3. Effect of different calcined catalysts on sulfur removal

Sulfur removal for photocatalytic oxidation of DBT with BaFe_2O_4 calcined in different temperatures photocatalysts in acetonitrile is shown in Fig. 7b. BaFe_2O_4 (calcined at 1000 $^\circ\text{C}$) exhibited relatively high activity. The conversion of DBT could reach 100%. The high activity of this catalyst might be attributed to higher purity.

3.6.4. Effect of the amount of the oxidant

To investigate the effect of the amount of the oxidant on the sulfur removal, various H₂O₂/sulfur (O/S) molar ratios at 30 °C with BaFe₂O₄ as the catalyst are shown in Fig. 8a. As can be seen, sulfur removal of DBT was 68% when the O/S was 1:1 in 40 min. With the O/S was increased from 2:1 to 3:1, the corresponding sulfur removal of DBT was up to 90%, 100% in 40 min, respectively. When the O/S molar ratio was 3:1, the sulfur removal of DBT could reach deep desulfurization. So only a stoichiometric ratio of 3:1 was chosen as the optimal ratio. To investigate the photocatalytic desulfurization performance of BaFe₂O₄ on different substrates, BT, DBT and RSH were studied.

3.6.5. Effect of different sulfur substrates on sulfur removal

As shown in Fig. 8b, the sulfur removal decreased in the order of DBT > BT > RSH at the same reaction conditions. Among the three aromatic sulfur compounds (BT, DBT), the activity was affected mainly by steric hindrance and electron density around the sulfur atom of sulfur compounds. The electron density on the sulfur atoms in DBT and BT was 5.758 and 5.739 respectively [34]. In the case of DBT and BT, the sulfur conversion increased with the increase of aromatic electron density. The desulfurization performance of two aromatic sulfur compounds was in the following order: DBT > BT > RSH as aliphatic compound was more easily oxidized than aromatic sulfur compounds. On the other hand, the steric hindrance of long alkyl chain of RSH was an obstacle for the approach of the sulfur atom to the catalytically active species. For the above reasons, the catalytic oxidation reactivity of the different substrates was in the following order: DBT > BT > RSH.

3.6.6. Recycling of catalytic system

Fig. 9 shows reusability of the catalyst in the oxidation of DBT. At the end of each run, the upper layer (model oil) was removed by decantation, and then the system was recharged with fresh H₂O₂ and model oil for the next run. Fig. 9 shows that this desulfurization system could be recycled seven times with a slight decrease in activity. Sulfur removal was 96.6%, 95.6, 92.9, 92.7, 91.5, 90.7, 88.0% respectively.

4. Conclusions

BaFe₂O₄ have been produced via hydrothermal technique by using PTSA. BaFe₂O₄ was synthesized at 800 °C , 900 °C and 1000 °C. Catalyst were dispersed in acetonitrile to oxidize sulfur-containing compounds with H₂O₂ under UV-Vis irradiation at room temperature. The effects of calcination temperature, catalyst concentration, and oxidant to sulfur (O/S) molar ratio were studied to optimize the reaction conditions. The BaFe₂O₄ photocatalyst had the highest photocatalytic desulfurization efficiency. The system containing BaFe₂O₄, acetonitrile, H₂O₂ could oxidize DBT to corresponding sulfone with desulfurization rate of 96.6% under UV-Vis irradiation. The photocatalytic reactivity of sulfur substrates decreased in the order of DBT>BT>RSH. The photocatalytic reaction could be recycled seven times with a slight decrease in sulfur removal, which might be developed into a promising, green, reproducible and environment-friendly process of photocatalytic desulfurization.

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Figure captions:

Fig. 1. SEM images of BaFe₂O₄ from **a** sample 1, **b** sample 2, **c** sample 3, **d** sample 4.

Fig. 2. SEM images of BaFe₂O₄ from **a** sample 4, **b** sample 5, **c** sample 6.

Fig. 3. XRD pattern of BaFe₂O₄ from **a** sample 4, **b** sample 5, **c** sample 6.

Fig. 4. FT-IR and EDS spectrum of BaFe₂O₄ obtained from sample 6.

Fig. 5. Magnetization versus applied magnetic field at room temperature for the obtained BaFe₂O₄ from sample 6.

Fig. 6. TEM images of barium monoferrite nanostructures.

Fig.7. Effect of BaFe₂O₄ on DBT removal with or without UV-Vis and Effect of catalysts calcined at different temperature on DBT removal. Experiment conditions: V(DBT)=5mL, m(catalyst) = 0.005 g, V(H₂O₂) = 16 μL, V(acetonitrile)=1 mL, T=30 °C, t = 2 h, UV-VIS.

Fig.8. Effect of different H₂O₂/sulfur (O/S) molar ratios on DBT removal and effect of different sulfur substrates on sulfur removal. Experiment conditions: V(DBT) = 5mL, m(catalyst) = 0.005 g, V(H₂O₂) = 16 μL, V(acetonitrile) = 1 mL, T = 30 °C, t = 2 h, UV-VIS.

Fig.9. Effect of recycling of the system. Experiment conditions: V(DBT)=5mL, m(BaFe₂O₄)=0.005g, V(H₂O₂)=16 μL, V(acetonitrile) = 1mL, T = 30 °C, t = 2 h, UV-VIS.

Table 1. Preparation conditions for samples 1–7.

Table 2. Sulfur removal of different photocatalytic desulfurization systems in model oil.

Table 1

Sample no.	Calcined of Temp ($^{\circ}\text{C}$)	Amount of PTSA / Ba	Morphology and Particle size
1	800	0	Irregular shapes; 300 nm
2	800	1:1	Irregular shapes; 50 nm- 500 nm
3	800	2:1	Hexagonal shapes; 200-400 nm
4	800	3:1	Hexagonal and uniform shapes; 100- 200 nm
5	900	3:1	
6	1000	3:1	-

Table 2

Entry	condition	Sulfur removal (%)
1	Catalyst + UV-Vis	1.8
2	Catalyst + H ₂ O ₂ + UV-Vis	4.4
3	Catalyst + acetonitrile + H ₂ O ₂ + UV-Vis	96.6
4	Catalyst + acetonitrile + UV-Vis	18.9
5	BaFe ₂ O ₄ + H ₂ O + H ₂ O ₂ + UV-Vis	1.3
6	Acetonitrile + H ₂ O ₂ + UV-Vis	25.2

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Fig .7.

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